Pacific Science (1975), Vol. 29, No. 2, p. 219–225
Printed in Great Britain

Trace Element Geochemistry of Biogenic Sediments from the Western Equatorial Pacific[1]

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ABSTRACT: Twenty-seven surface samples of biogenic sediment, including radiolarian, nannofossil, and foraminiferal oozes from the Western Equatorial Pacific have been analyzed for potassium, magnesium, iron, rubidium, strontium, barium, chromium, cobalt, nickel, copper, and zinc by rapid instrumental techniques. Interelement associations have been evaluated with the use of a computer-compiled matrix of correlation coefficients. The variables considered include elemental determinations, water depth, and percentage of calcium carbonate. The associations calcium carbonate:strontium, potassium:rubidium, and barium:nickel:copper may all be explained with regard to their mode of entry into the sediment. The data indicate that organic fixation of metals is a significant process during the deposition of Pacific Equatorial sediments, whereas contributions from other sources, i.e., sorbed cations on the surfaces of clays and coprecipitation with iron or manganese oxides, are effectively masked in most cases by high rates of biogenous deposition.

THE FLOOR of the Equatorial Pacific between the Line Islands (about 155° W) and the Ontong Java Plateau (about 155° E) is characterized by a thick sequence of biologically derived sediments. Foraminiferal and nannofossil oozes dominate areas above about 4,800 m, whereas radiolarian oozes are prevalent below this depth. Trace element data for biogenous sediments are scanty, particularly from this region. The majority of elemental data reported in the literature (Goldberg and Arrhenius 1958, el-Wakeel and Riley 1961, Young 1968, and Cronan 1970) deal with samples from the eastern or northeastern Pacific. Twenty-seven biogenic sediment samples from the tops of cores taken by the research vessels of the Hawaii Institute of Geophysics have been used for this study. All samples except one were located within 10° of the equator (Figure 1). Locations, depth, and sediment type are presented in Table 1.

The purpose of this communication is threefold: (1) to report elemental abundances of the rare metals Rb, Sr, Ba, Cr, Co, Ni, Cu, and Zn in biogenous sediments from the Western Equatorial Pacific, (2) to evaluate interelement associations by linear regression techniques, and (3) to assess mechanisms that are operative in the fixation of trace elements into biogenic sediment.

I would like to express thanks to the scientific party and crew of the research vessels of the Hawaii Institute of Geophysics for obtaining the samples used in this study. Drs. Robert M. Garrels, Pow-Foong Fan, Charles Fein, and James Andrews provided helpful comments on the manuscript.

ANALYTICAL METHODS

All elements reported in this study were determined by rapid instrumental techniques. Fe, Mg, K, Co, Cr, Cu, and Zn were analyzed by atomic absorption spectrophotometry (AA). Sample dissolution was achieved by the HF-H_3BO_3 system as described by Bernas (1968). All atomic absorption measurements were

[1] Financial support was provided by the United States Navy, Office of Naval Research, contract N00014-70-A-0016-001. Hawaii Institute of Geophysics contribution no. 590. Manuscript received 20 June 1974.

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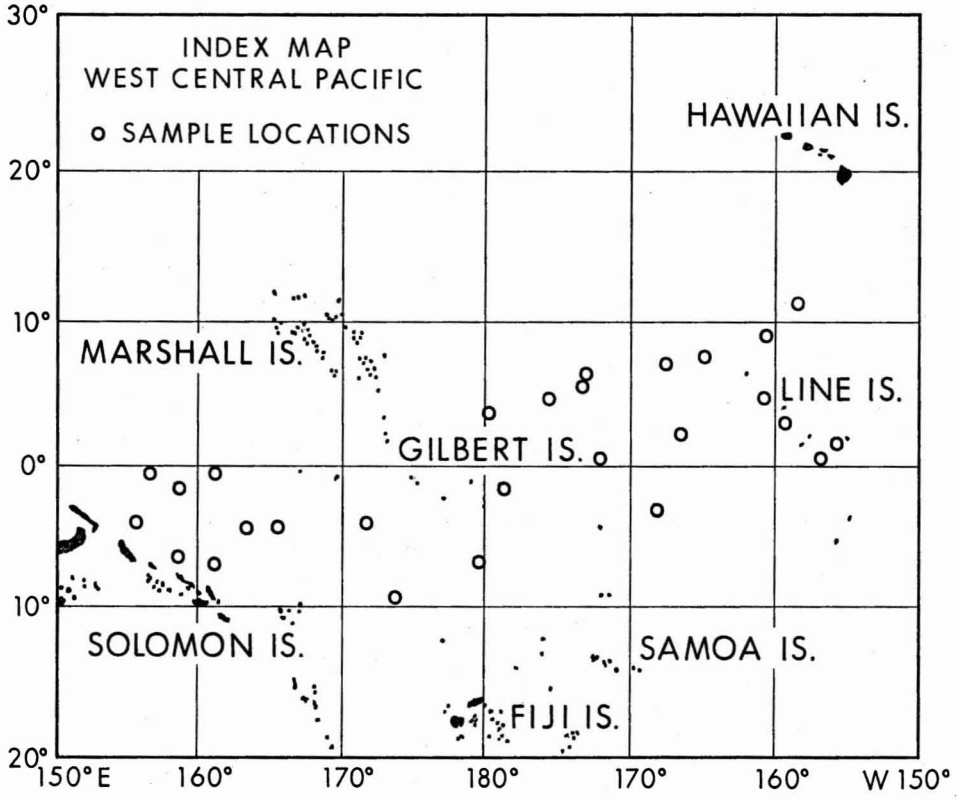

FIGURE 1. Locations of surface sediments used in this study.

carried out on a Perkin-Elmer model 303 spectrophotometer under recommended instrumental conditions. Rb, Sr, Ba, and Ni were analyzed by X-ray fluorescence spectrometry (XRF). Powdered and dried samples were briquetted with methyl cellulose as a binder and boric acid as a backing. This method of preparation proved to be satisfactory in that the briquettes possessed adequate mechanical strength to ensure the stability of the sample when the sample was used in a vacuum; and, when a sample was diluted with a standard additive, the differences in sample composition or "matrix" effects were somewhat buffered. All X-ray determinations were made on a Norelco universal vacuum spectrograph with instrumental conditions optimized for each element. Calibration for AA and XRF analyses was achieved with both synthetically prepared standards and United States Geological Survey rock standards. A gas volumetric system was used for the determination of weight percent $CaCO_3$. The apparatus, designed by Hülsemann (1966) consists essentially of a gas generating system connected to a manometer on which the volume of CO_2 can be read by the displacement of a column of mercury. Details of all analytical techniques, including a discussion of interelement interferences, precision, and accuracy, have been presented elsewhere (Burnett 1971*a*). All elemental determinations from this study are presented in Table 2.

RESULTS AND INTERELEMENT ASSOCIATIONS

The 13-variable matrix of correlation coefficients presented here (Table 3) is based on 27 samples, with a provision in the computer program for disregarding missing data. Relations were established between individual trace elements; correlations were also checked between the rare metals and the major elements K, Mg, and Fe; percent $CaCO_3$; and water depth. The elemental concentrations have not

TABLE 1

LOCATION OF SAMPLES STUDIED

HIG LOG NUMBER*	GEOGRAPHIC POSITION	DEPTH (M)	SEDIMENT TYPE
S68-PC-1	11°03′ N, 158°00′ W	5,150	siliceous ooze
S68-PC-28	08°55′ N, 160°34′ W	4,805	siliceous ooze
S68-PC-29	07°40′ N, 164°50′ W	4,970	siliceous ooze
S68-PC-30	07°00′ N, 167°31′ W	4,775	siliceous ooze
S68-PC-35	06°11′ N, 173°01′ W	4,890	nannofossil ooze
S68-PC-31	05°27′ N, 173°05′ W	5,740	siliceous ooze
S68-PC-34	04°43′ N, 175°18′ W	5,100	siliceous ooze
LIR-1-004	04°40′ N, 161°00′ W	na†	foraminiferal ooze
S68-PC-33	03°52′ N, 179°32′ W	5,428	siliceous ooze
LIR-1-011	03°00′ N, 159°17′ W	na	foraminiferal ooze
S68-PC-27	02°15′ N, 166°31′ W	5,520	nannofossil chalk ooze
LIR-1-006	01°40′ N, 155°36′ W	na	foraminiferal ooze
S68-PC-25	00°35′ N, 172°11′ W	5,620	siliceous ooze
LIR-1-008	00°15′ N, 156°34′ W	na	foraminiferal ooze
S68-PC-11	00°26′ S, 158°17′ E	3,900	nannofossil chalk ooze
S68-PC-12	00°52′ S, 161°13′ E	3,430	nannofossil-foram ooze
S68-PC-16	01°36′ S, 158°46′ E	2,020	foram chalk ooze
S68-PC-24	02°03′ S, 178°45′ W	5,273	siliceous ooze
S68-PC-02	03°48′ S, 168°11′ W	5,520	siliceous ooze
S68-PC-18	04°13′ S, 155°36′ E	2,580	nannofossil-foram chalk ooze
S68-PC-21	04°20′ S, 172°04′ E	3,875	siliceous nannofossil ooze
S68-FFC-26	04°44′ S, 163°29′ E	2,240	foram chalk ooze
S68-FFC-34	04°55′ S, 165°41′ E	2,850	nannofossil chalk ooze
S68-FFC-15	07°00′ S, 158°11′ E	2,475	nannofossil chalk ooze
S68-PC-06	07°15′ S, 161°17′ E	1,628	nannofossil chalk ooze
S68-PC-03	07°06′ S, 179°50′ E	5,450	siliceous ooze
S68-PC-04	09°07′ S, 173°50′ E	5,250	siliceous ooze

* Sample designation as recorded on research vessels of the Hawaii Institute of Geophysics.
† na = not available.

been recalculated to a calcium-carbonate-free basis, as is commonly done when minor element abundances in marine sediments are being reported (Turekian and Imbrie 1966). It was an objective of this work to determine if the metals being considered here are associated with the organic fraction of the sediment. It did not seem reasonable, therefore, to exclude carbonate from the sediments under consideration.

A major drawback to utilization of correlation coefficients when considering a suite of variables with a finite summation (100 percent in the case of a chemical analysis) is that negative coefficients may tend to be enhanced simply as a result of the increased concentrations of one or more of the components. This effect should be minimal in the case of trace elements as their absolute abundance is low, therefore does not contribute significantly to the total. This effect is evident, however, in the case of $CaCO_3$, which produces a negative correlation with every variable except Sr, which substitutes quite readily in the calcite lattice (Turekian and Kulp 1956, Turekian 1964). Note also that $CaCO_3$ and Sr are the only variables that display a negative correlation with respect to depth.

One of the strongest interelement correlations shown in Table 3 is that between K and Rb. This relationship is known to occur in geochemical materials of all types. Ahrens, Pinson, and Kearns (1952) have reported that the "normal" K:Rb ratios in igneous rocks and meteorites range between 115–460 with an average of 230. The carbonate ooze samples have generally lower K:Rb values, with a mean of 159. The siliceous sediments have

TABLE 2

CHEMICAL COMPOSITION OF SURFACE SEDIMENTS FROM THE WESTERN EQUATORIAL PACIFIC

HIG LOG NUMBER*	$CaCO_3$ (%)	MgO (%)	K_2O (%)	Fe_2O_3† (%)	Rb (ppm)	Sr (ppm)	Ba (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)
					CARBONATE OOZES							
S68-PC-35	72	1.07	0.25	0.63	16	760	850	20	9	15	76	79
LIR-1-004	93	0.61	0.06	0.08	nd	1,000	310	nd	19	nd	23	8
LIR-1-011	99	0.86	0.09	0.20	nd	1,100	460	nd	19	nd	26	20
S68-PC-27	85	1.28	0.25	0.75	18	1,100	500	13	20	11	55	120
LIR-1-006	93	0.80	0.15	0.45	nd	1,200	480	5	20	14	42	10
LIR-1-008	89	0.95	0.15	0.36	nd	1,200	370	8	19	14	43	63
S68-PC-11	85	1.25	0.24	1.28	18	1,100	370	nd	22	15	57	62
S68-PC-12	85	0.99	0.25	0.96	18	1,100	490	32	10	17	45	250
S68-PC-16	94	1.08	0.15	0.84	15	1,000	280	20	13	11	26	160
S68-PC-18	42	1.53	1.59	2.89	32	900	560	50	39	21	50	50
S68-PC-21	83	1.29	0.32	1.71	15	1,100	460	nd	32	18	75	180
S68-FFC-26	93	0.74	0.13	0.74	15	1,000	280	nd	10	14	47	78
S68-FFC-34	86	1.00	0.21	1.04	nd	1,000	550	16	10	14	36	20
S68-FFC-15	53	2.03	0.62	3.60	24	900	530	nd	45	19	78	88
S68-PC-06	79	1.56	0.32	2.02	nd	1,100	440	nd	16	18	36	57
Av. Carb.	82	1.14	0.32	1.17	19	1,000	720	20	20	15	48	83
					SILICEOUS OOZES							
S68-PC-1	0.7	3.43	2.81	7.10	100	250	2,400	55	98	190	420	210
S68-PC-28	5.1	3.57	2.27	5.23	77	370	4,300	36	64	180	410	220
S68-PC-29	16.9	2.93	2.08	4.55	76	420	2,500	60	30	120	290	200
S68-PC-30	26.1	2.45	1.44	3.38	63	440	3,000	25	18	150	340	140
S68-PC-31	0.3	3.42	2.32	5.70	79	190	1,600	30	44	150	265	100
S68-PC-34	1.4	4.67	1.66	6.69	57	400	6,000	31	55	350	550	240
S68-PC-33	0.8	3.58	1.99	6.23	83	190	1,000	90	63	130	330	100
S68-PC-25	0.7	2.86	1.91	5.56	73	200	1,200	63	51	120	300	200
S68-PC-24	0.5	4.12	1.24	5.25	50	210	780	71	73	160	360	370
S68-PC-02	0.0	4.13	2.11	9.24	72	260	870	110	50	100	300	130
S68-PC-03	0.4	4.18	2.16	9.98	68	240	910	60	74	190	380	130
S68-PC-04	1.1	4.16	1.49	11.13	41	270	720	50	60	190	490	150
Av. Sili.	4.5	3.62	1.96	6.69	70	290	2,000	57	57	170	370	180
Tech.	GAS	AA	AA	AA	XRF	XRF	XRF	AA	AA	XRF	AA	AA
Est. Prec.	3%	2%	2%	2%	10%	10%	10%	10%	10%	10%	10%	10%

NOTE: Units are in weight percent and parts per million (ppm) by weight. The following abbreviations have been used in this table—Av. Carb., average carbonate ooze from this study; Av. Sili., average siliceous ooze from this study; Tech., analytical technique used; GAS, gas volumetric technique; AA, atomic absorption spectrophotometry; XRF, X-ray fluorescence spectrometry; nd, not detected; Est. Prec., estimated precision.

* Sample designation as recorded on research vessels of the Hawaii Institute of Geophysics.

† Total iron reported as Fe_2O_3.

values more common to crustal material, i.e., a mean of 233 compared to Taylor's (1964) crustal K:Rb average of 232. K:Rb values reported by Burnett (1971*b*) for Pacific brown clays were also close to various estimates for crustal rocks. The data suggest that Rb closely follows K in most types of marine sediments, but a partitioning effect between these two elements is evident in calcareous oozes. An enrichment of Rb relative to K appears to occur during carbonate deposition in the Equatorial Pacific.

The correlation coefficients for Ba indicate that this element is related more closely to the trace elements Ni and Cu than to the more geochemically similar elements Ca and K. The correlation of Ba:Ni:Cu is not interpreted here as an association within a common phase (a situation which would lead to high correlation coefficients; see Chave and Mackenzie 1961)

TABLE 3

CORRELATION MATRIX OF 27 BIOGENIC SEDIMENTS FROM THE WESTERN EQUATORIAL PACIFIC

	DEPTH	$CaCO_3$	MgO	K_2O	Fe_2O_3	Rb	Sr	Ba	Cr	Co	Ni	Cu	Zn
Depth	1.000												
$CaCO_3$	−0.733	1.000											
MgO	0.704	−0.955	1.000										
K_2O	0.658	−0.943	0.860	1.000									
Fe_2O_3	0.625	−0.906	0.937	0.835	1.000								
Rb	0.663	−0.884	0.773	0.959	0.697	1.000							
Sr	−0.772	0.972	−0.920	−0.908	−0.873	−0.884	1.000						
Ba	0.127	−0.437	0.484	0.439	0.301	0.521	−0.364	1.000					
Cr	0.411	−0.731	0.683	0.674	0.719	0.540	−0.724	−0.004	1.000				
Co	0.566	−0.840	0.841	0.820	0.827	0.735	−0.787	0.277	0.630	1.000			
Ni	0.644	−0.851	0.905	0.768	0.784	0.714	−0.819	0.642	0.374	0.732	1.000		
Cu	0.721	−0.918	0.945	0.834	0.873	0.773	−0.910	0.563	0.512	0.799	0.965	1.000	
Zn	0.417	−0.570	0.606	0.468	0.456	0.280	−0.557	0.340	0.357	0.532	0.564	0.627	1.000

but a response to a similar mode of fixation of these elements in biogenic sediments. The covariance of Ba with Cu in organically produced marine sediments was first noted by Revelle et al. (1955: 221–236) with further observations by Goldberg and Arrhenius (1958) and Turekian and Tausch (1964). Turekian and Imbrie (1966) noted an association between Cu and the calcium carbonate fraction of sediments from the Atlantic. Although this relation is not apparent here, organic fixation of Cu is still considered to be significant in these deposits. The addition to, or redistribution of, rare metals such as Ni in pelagic sediments by organic molecules has been suggested by Baturin and Kochenov (1967). The incorporation of Ni and Cu into some type or types of organic complexes that are not completely disassociated on their descent to the ocean floor is perhaps a reasonable, although very incomplete, explanation of their fixation in biogenic sediments. These organic molecules may be related to the organic coating on carbonate tests reported by Chave (1965) and Suess (1968). In addition, Ba often occurs as barite, which is present in moderate to high concentrations in some equatorial sediments of the Pacific (Arrhenius and Bonatti 1965). The production of $BaSO_4$ crystals has been attributed to an association with planktonic productivity (Turekian 1968).

Cr and Co apparently are related to the "clay" fraction of the sediment, showing higher correlations to Fe, K, and Mg than to other trace elements. The distribution of Zn is curious, its concentration apparently being independent of the other variables reported except for a slight correlation with Cu. Unlike the other transitional metals reported in Table 3, Zn does not show as strong a negative variance with respect to the calcium carbonate content.

RARE METAL FIXATION IN BIOGENIC SEDIMENTS

Several mechanisms have been proposed in the past for trace element enrichment in marine sediments. Turekian (1968) has suggested that very fine-grained pelagic material has the ability to absorb a large number of metallic cations due to its large surface area. Nicholls (1967) has considered the influence of pressure in controlling trace element concentrations. He concluded that the dependence on pressure is too small and inadequate to explain the observed trace element content in pelagic deposits.

The sedimentary deposits of the Equatorial Pacific, being a composite of organically produced constituents, eolian transported materials, and authigenic components, must have several mechanisms that are operative in the fixation of metallic elements into the various sediment types. Metals such as Cu and Ni probably enter the sediment as immobile metallo-organic complexes. Others may be introduced as sorbed cations on the surfaces of clay minerals and be redistributed after deposi-

tion. Bonatti et al. (1971) have suggested that redox reactions may account for the post-depositional migration of many trace elements in the sediment column during diagenesis. A minor element occurring as a major element of a mineral, such as Ba and Sr in a celestobarite phase or Ba in harmotome, may substantially affect trace element distributions. Apparently this is not an important factor here, as the absolute abundance of Ba is low; and if the production of barite is related to the dissolution of carbonate tests, a stronger negative covariation of Ba with $CaCO_3$ would be expected. The occlusion of the transitional metals Ni, Co, Cu, and Zn with precipitating Fe or Mn oxides may account for a substantial fraction of these elements in pelagic sediments (Chester and Hughes 1966). The contribution of metals in this manner is effectively masked in the shallower areas of the Equatorial Pacific by a high influx of carbonate sedimentation. Submarine volcanism has been suggested as a potential source for these trace elements (Bonatti and Nayudu 1965), but organic fixation with subsequent redistribution within the sediment may be more important in areas of high organic productivity.

The suggested mechanisms for trace element fixation probably occur in nearly all types of pelagic sediments, differences being a matter of degree rather than of kind. These mechanisms should be fairly independent of each other and may occur in various combinations. The deciding factors appear to be the regional and environmental situations in which the sediments are deposited. More specifically, such factors as depth, rate of supply, productivity, and proximity to volcanism are responsible for determining the dominant mode of fixation of trace elements in pelagic sediments.

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